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AN INTER-LABORATORY ANALYTICAL STUDY ON THE ANALYSIS OF GOLD IN COPPER ANODE SLIMES

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by

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ABSTRACT

Traditional fire assay and dissolution/spectroscopic techniques were compared for the analysis of gold in the copper anode slimes laboratory standard, KCAS-1. Both methods yielded similar inter-laboratory means and standard deviations. Umpire laboratories traditionally used by the copper refining industry all reported values lower than the grand means calculated for both the fire assay and dissolution/spectroscopic methods.

Keywords: copper anode slimes, gold analysis, fire assay, ICAP, DCAP, FAAS, umpire analysis

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INTRODUCTION

Copper anode slimes typically contain major amounts of silver and gold, trace quantities of platinum, palladium, transition metals and other impurities. Fire assay methods are customarily used to determine the gold content of copper anode slimes. However, experienced fire assayers are rapidly becoming a rare breed with few or no replacements available, specialized and expensive facilities are required to house fire assay equipment, and the furnaces used exhibit non-uniform temperature profiles. These issues, compounded by manpower shortages in the analytical laboratories and lengthy analysis times for fire assay procedures, prompted an evaluation of alternative methods for the analysis of gold in copper anode slimes.

In 1988, a group of analytical chemists from copper refineries in Canada and the United States was assembled to investigate the quality of the data emerging from the analytical laboratories. Since then a number of inter-laboratory analytical studies have been performed and several problems have been discovered. In a few cases, new or alternative analytical methods have been implemented. Within this framework, this study will focus on a comparison between traditional fire assay methods and wet dissolution/spectroscopic techniques for the determination of gold in copper refinery anode slimes. Umpire laboratories were included in this study at the request of the industry. Some of the participating industrial laboratories solicited the voluntary involvement of the umpire laboratories.

Participating Laboratories

CANMET acted as the convener for the study and the following laboratories provided analytical data:

Industrial Laboratories

Copper Range Company, White Pine, Michigan
Gaston Copper Recycling Company, Gaston, South Carolina
Inco Limited, Central Laboratory, Copper Cliff, Ontario
Inco Limited, Copper Refinery, Copper Cliff, Ontario
Inco Limited, J. Roy Gordon Research Laboratory, Mississauga, Ontario
Kennecott, Utah Copper Refinery, Magna, Utah
Magma Copper Company, San Manuel, Arizona
Kidd Creek Division, Falconbridge Limited, Timmins, Ontario
CCR Refinery, Noranda Copper Smelting and Refining, Montreal-Est, Québec
Phelps Dodge Refining Corporation, El Paso, Texas
Southwire Company, Copper Division, Carrollton, Georgia

Umpire Laboratories

Walker and Whyte, Long Island City, New York
Umpire and Control Services Inc., West Babylon, New York
Alfred H. Knight Laboratories, Ltd., Pompton Lake, New Jersey
Ledoux and Co., Teaneck, New Jersey

SAMPLE PREPARATION

Although the procedure for preparing the anode slimes was described elsewhere (1), it will be reviewed here. The copper anode slimes were supplied by the Kidd Creek Division of Falconbridge Ltd., and the copper and lead were removed by traditional processes. At CANMET the bulk sample, ~10 kg, was washed 5 times with deionized water, filtered, air dried overnight and vacuum dried for 24 hours. The material was blended for 16 hours in a conical blender and individual 55 ± 5 g samples were weighed into glass jars. The jars were then sealed under argon by placing them in a glove box and purging 3 times with argon. Bottles were individually sealed in mylar bags under nitrogen.

Each laboratory was supplied with one bottle of sample and was requested to analyze the sample for Au in duplicate on 5 consecutive days. This protocol was suggested by participants in the inter-laboratory study and was felt to give a realistic estimation of within-laboratory and inter-laboratory standard deviations. The participating laboratories

determined the method for analysis (e.g., fire assay, ICAP, etc.) and in some cases the laboratories were performing a non-routine analysis.

STATISTICAL ANALYSIS

Gold values expressed as troy ounces per short ton were converted to ppm via the conversion factor 34.2857. Each data set was examined by Cochran's test for laboratory variance. This test stipulates that a set of results submitted by a laboratory is an outlier if the laboratory variance is large compared to the other laboratories (2). This quantity is calculated as follows:

$$C_{calc} = \frac{S_i^2 \text{ max}}{\sum_{i=1}^{i=k} S_i^2} \qquad (1)$$

Where 'S_i' is the observed within laboratory variance and '$S_{i\ max}$' is the maximum within-laboratory variance. The data set is rejected if the computed value of 'C_{calc}' is larger than a critical value, 'C_{crit}', for the given number of replicates and data sets. In cases where the number of replicates originating from each laboratory was not equivalent, an average value was computed. Dixon's test for between-laboratory means was also applied to both data sets. This test stipulates that the mean result from a laboratory is an outlier if it is too far from the other laboratory means. Data sets identified as Cochran outliers, which are normally reinstated for the application of Dixon's, test were not included for this study. The mean values are sorted into ascending order and the value of r_{mn} is calculated according to the following guidelines;

r_{mn}	If y_k is Suspect	If y_1 is Suspect	Range of k
r_{10}	$(y_k-y_{k-1})/(y_k-y_1)$	$(y_2-y_1)/(y_k-y_1)$	$k \leq 7$
r_{11}	$(y_k-y_{k-1})/(y_k-y_2)$	$(y_2-y_1)/(y_{k-1}-y_1)$	$8 \leq k \leq 12$
r_{22}	$(y_k-y_{k-1})/(y_k-y_3)$	$(y_3-y_1)/(y_{k-2}-y_1)$	$k > 12$

where 'k' is the number of mean values.

Additional statistical calculations included within-laboratory and inter-laboratory means, standard deviations and relative standard deviations.

RESULTS AND DISCUSSION

Laboratories were arbitrarily assigned numbers and each laboratory was informed of its performance. Umpire laboratories were identified only to the industrial laboratories which requested their participation. The data were categorized into fire assay and spectroscopic results. Spectroscopic results include those using a fusion or wet chemical dissolution first step followed by an ICAP, DCAP or FAAS finish.

The raw data for the fire assay and spectroscopic techniques are illustrated in Figures 1 and 2, respectively. Data identified as outliers are represented by filled boxes. Solid lines on the plots indicate the calculated grand means, excluding outliers. The raw values submitted for the Au content range from 1980 ppm to 2094 ppm for fire assay and from 1970 ppm to 2066 ppm for the dissolution/spectroscopic results. Summary statistics are presented in Tables I and II for fire assay and dissolution/spectroscopic results, respectively. Rejected data sets are enclosed by boxes. Cochran's variance test revealed one outlying fire assay data set and one outlying spectroscopic data set as illustrated in Table III. Laboratory 1, identified as a Cochran outlier also recommended that the data be excluded since 2 or 3 different analysts were used over the 5-day analysis period. This data set was therefore not included in the calculation of Dixon outliers. Dixon's test for inter-laboratory means did not reveal any outliers in the fire assay data. The spectroscopic data also did not yield any true Dixon outliers. However, laboratory 5 was identified as an outlier on the following grounds. A mean Au concentration of 2047 ppm was reported during the last inter-laboratory study (1) which is not consistent with the data presented here. Also, application of Dixon's test gave an r_{10} value of 0.552, less than the critical value of 0.569. The inconsistency of the data and the results of Dixon's test were used to identify laboratory 5 as an outlier.

The two sets of data submitted by laboratory 10 for fire assay are for 2 different bottles of sample. Fire assay results yielded within-laboratory standard deviations ranging from a minimum of 4.3 ppm to a maximum of 22.0 ppm. Spectroscopic analysis produced a range of within-laboratory standard deviations of 6.2 ppm to 23.9 ppm. A grand mean of 2037 ppm and an inter-laboratory standard deviation of 26 ppm were realized from the fire assay data. Similarly, a grand mean of 2042 ppm and an inter-laboratory standard deviation of 17 ppm were realized for the spectroscopic analyses. This suggests that dissolution/ spectroscopic analysis yields comparable data to fire assay techniques. Strict protocol was not invoked for either the fire assay or spectroscopic methods. Thus, some of the fire assay data are proof-corrected whereas others are not, but this may not be a large contributing factor to the observed inter-laboratory standard deviation. Since each laboratory was requested to use routine procedures, a non-routine procedure (e.g., proof-corrected) imposed on one or more laboratories may actually increase the inter-laboratory standard deviation.

Laboratory 14 performed 2 different dissolution techniques on the same sample followed by a FAAS finish. The technique yielding the lower Au content employed an initial filtration step immediately following a nitric acid dissolution step. Although the filter paper was completely decomposed in a subsequent step, the data suggest a loss of Au during the process. Hence, a standardized dissolution technique would undoubtedly produce a lower standard deviation for techniques employing a spectroscopic finish. Laboratories 4 and 5 submitted data for both techniques (i.e., fire assay and spectroscopic), and found similar within-laboratory standard deviations in each instance.

The Au concentration, as measured by fire assay, appears to increase slightly over the 5-day measuring period as illustrated in Figure 3. The lack of a similar trend with the spectroscopic data and previous conclusions regarding sample stability (1) suggest that a methodological factor may be involved.

The marketable value of anode slimes shipments are determined via contractual splitting limits. These limits represent the maximum amount of disagreement admissible

between the analytical determinations of the buyer and the seller. A typical splitting limit for Au, in copper anode slimes, is 0.5% of the lower assay. Using a value of 2035 ppm Au a splitting limit of 10 ppm Au can be calculated. This implies that the laboratory exhibiting the higher determined Au value must agree within 10.0 ppm of the other laboratory, otherwise an umpire laboratory is used. The actual value of the slimes shipment, relative to the Au content only, would then be the median value between the buyer and seller determinations. The financial risk to either party is therefore approximately 5 ppm of Au. Thus, an estimated maximum within-laboratory standard deviation of 10 ppm is desirable for Au in copper anode slimes shipments. The analytical data in Tables I and II indicate that with the present technology using the conditions employed in this study, less than 40% of the laboratories involved can achieve this level of precision. It should be remembered, however, that splitting limits are contractual agreements designed to protect the interests of both the buyer and the seller. Thus, although splitting limits often appear unreasonable to an analyst, they are justifiable when other factors are considered.

Although the day-to-day variance added to the overall standard deviation for both fire assay and spectroscopic techniques, the host of different dissolution/spectroscopic techniques employed for the spectroscopic analyses certainly was a major contributor to the grand standard deviation. This is readily observed in the data submitted by laboratory 14 which used 2 different dissolution methods and produced mean Au concentrations differing by 22 ppm. If a standardized wet chemical dissolution technique was adopted, the within-laboratory and indeed the inter-laboratory standard deviation should improve markedly.

The performance of umpire laboratories in the copper refining industry is of considerable significance. Laboratories which are routinely employed in the copper refining industry were included in the study on a voluntary basis at the request of the industry. Without exception, the results submitted by the umpire laboratories were below the grand means observed by both fire assay and dissolution/spectroscopic techniques. Since complete data on the analytical techniques used by the umpires are not available, the reasons for this are unclear. However, further investigation of the cause may be warranted.

CONCLUSIONS

The analysis of anode slimes by spectroscopic techniques using a variety of sample decomposition methods yielded similar results as those obtained from traditional fire assay techniques. A wet dissolution or fusion decomposition of the anode slimes followed by a spectroscopic finish would most certainly be faster and more facile than a traditional fire assay approach. This is particularly true if proof corrections are incorporated into the fire assay procedure. Although the inter-laboratory standard deviations for both procedures were on the order of 17-26 ppm, these are not excessive considering that a single analytical protocol was not used for either method. This study was not designed to determine absolute levels of precision and accuracy but to compare the results of the fire assay and dissolution/ spectroscopic techniques for the analysis of copper anode slimes. In this regard, spectroscopic methods provided analytical data of equal calibre to traditional fire assay techniques. Although the within-laboratory and inter-laboratory standard deviations were large, the use of a single, agreed upon dissolution technique should eliminate a large portion of the variance. Therefore, further studies may be directed toward the development of a standardized dissolution technique for use with spectroscopic techniques. The methods employed by laboratory 14 offer a good point of reference.

Results supplied by the umpire laboratories were satisfactory, although each umpire laboratory reported results lower than the grand standard deviations of both techniques. Also, 8 of the 11 industrial laboratories reported Au concentrations higher than the umpire laboratories. Assuming that each laboratory used its regular in-house method for the Au determination of the anode slimes, this suggests that in 73% of the cases involving umpire laboratories, the ruling would be in favour of the industrial laboratory reporting the lower result.

REFERENCES

1. Weatherell C.J., "Inter-laboratory Analytical Studies in the Copper Refining Industry", Copper 91 - Volume III, W.C. Cooper, D.J. Kemp, G.E. Lagos and K.G. Tan, Eds., Pergamon Press, Oxford, 1991, 425-447.

2. Sutarno, R., "Procedure for Statistical Evaluation of Analytical Data Resulting from International Tests", Standards Association of Australia, ISO/TC 183 Report N201E, 1987.

Table I - Summary Statistics for the Analysis of Gold in the Copper Anode Slimes Sample, KCAS-1, by Fire Assay

Laboratory Number	Mean (ppm)	Std. Dev. (ppm)	RSD (%)
1	1941	58.1	3.0
2	2050	18.8	0.9
3	2038	22.0	1.1
4	2057	4.4	0.2
5	2025	10.6	0.5
6	2087	4.3	0.2
7	2030	19.8	1.0
8	2023	21.9	1.1
9	1997	5.8	0.3
10	2035	11.0	0.5
10	2036	13.5	0.7
11	2030	5.9	0.3
Grand Mean		2037 ppm	
Grand Std. Dev.		26 ppm	
Grand RSD		1.3 %	

Table II - Summary Statistics for the Analysis of Gold in the Copper Anode Slimes Sample, KCAS-1, by Dissolution/Spectroscopic Methods

Laboratory Number	Mean (ppm)	Std. Dev. (ppm)	RSD (%)
12	2040	7.2	0.4
5	1995	13.5	0.7
4	2032	13.0	0.6
14	2040	15.0	0.7
14	2062	6.2	0.3
13	2042	23.9	1.2
15	1915	40.9	2.1
Grand Mean		2042 ppm	
Grand Std. Dev.		17 ppm	
Grand RSD		0.8 %	

Table III - Evaluation of the Analytical Data by Cochran's Test for Maximum Variance

Method	Iteration	C_{calc}	C_{crit}	n	k	Lab Rejected
Fire Assay	1	0.602	0.239	10	12	1
	2	0.217	0.260	10	11	--
Spectroscopic	1	0.574	0.410	9	7	15
	2	0.461	0.469	9	6	--

n = average number of replicates
k = number of data sets
α = 0.01

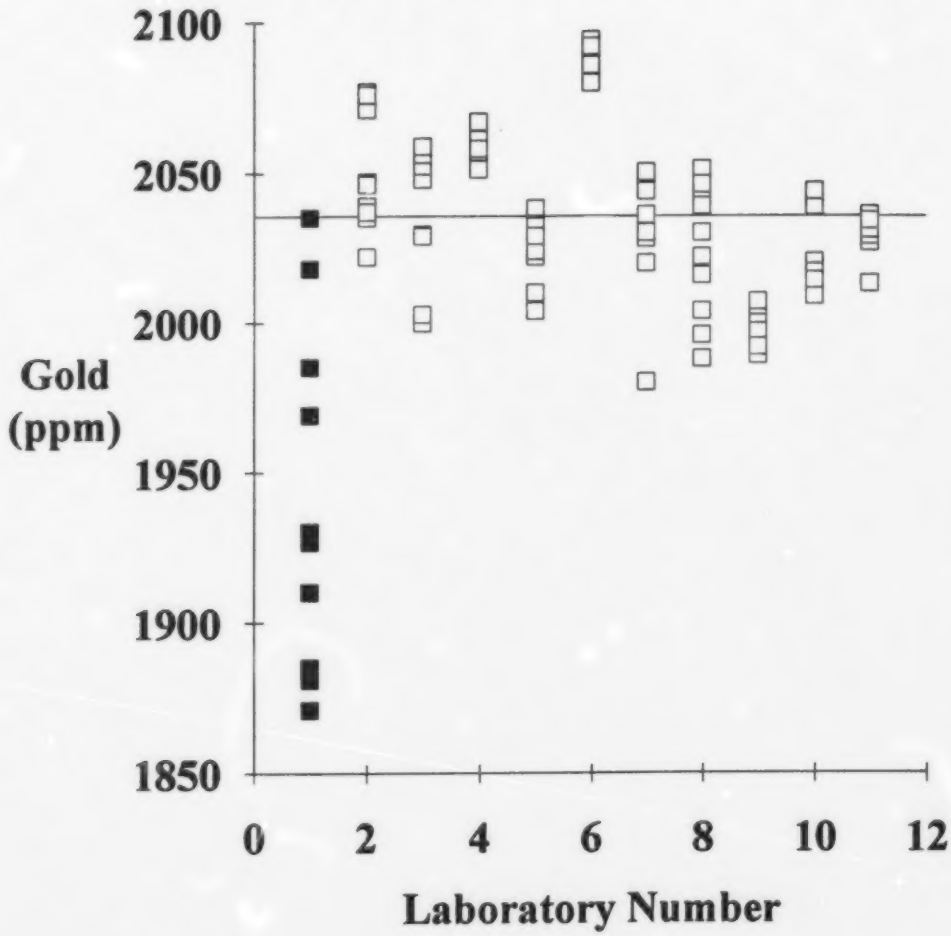

Figure 1. Raw Data for the Analysis of the Copper Anode Slimes Sample, KCAS-1, by Fire Assay

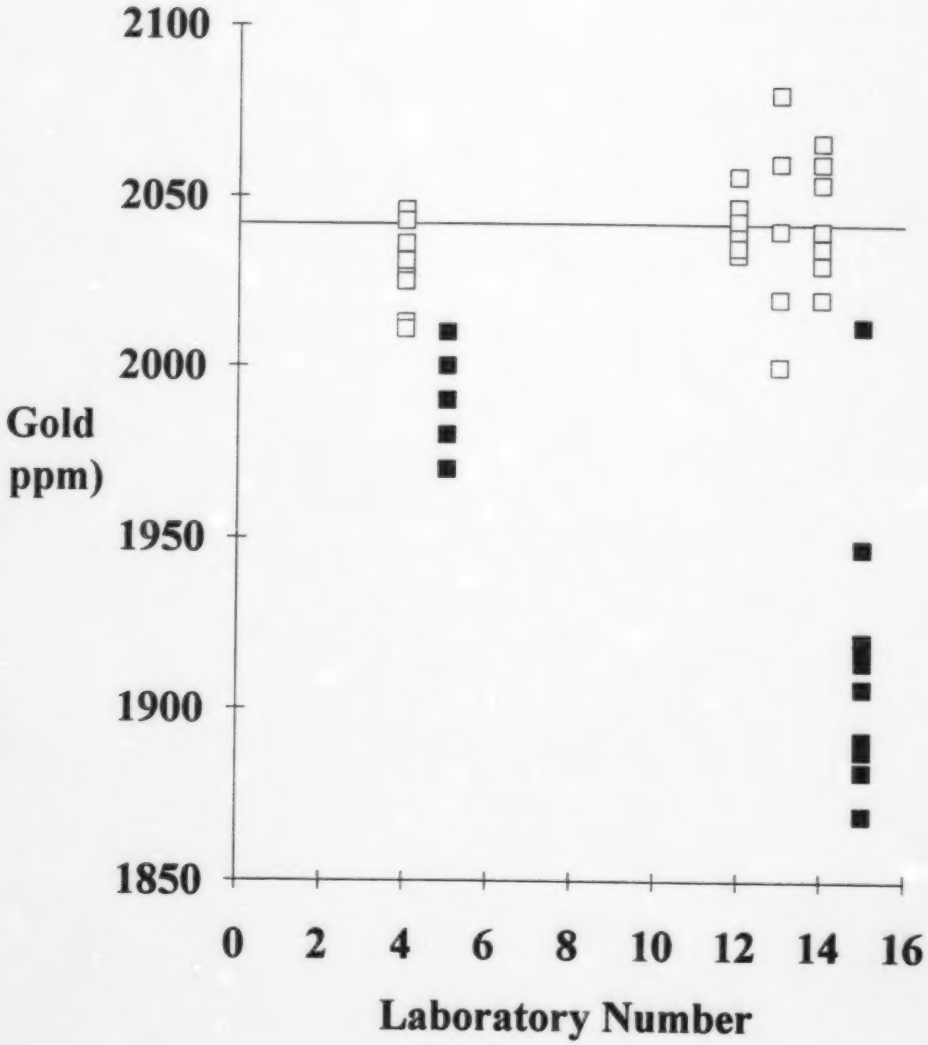

Figure 2. Raw Data for the Analysis of the Copper Anode Slimes Sample, KCAS-1, by Spectroscopic Techniques.

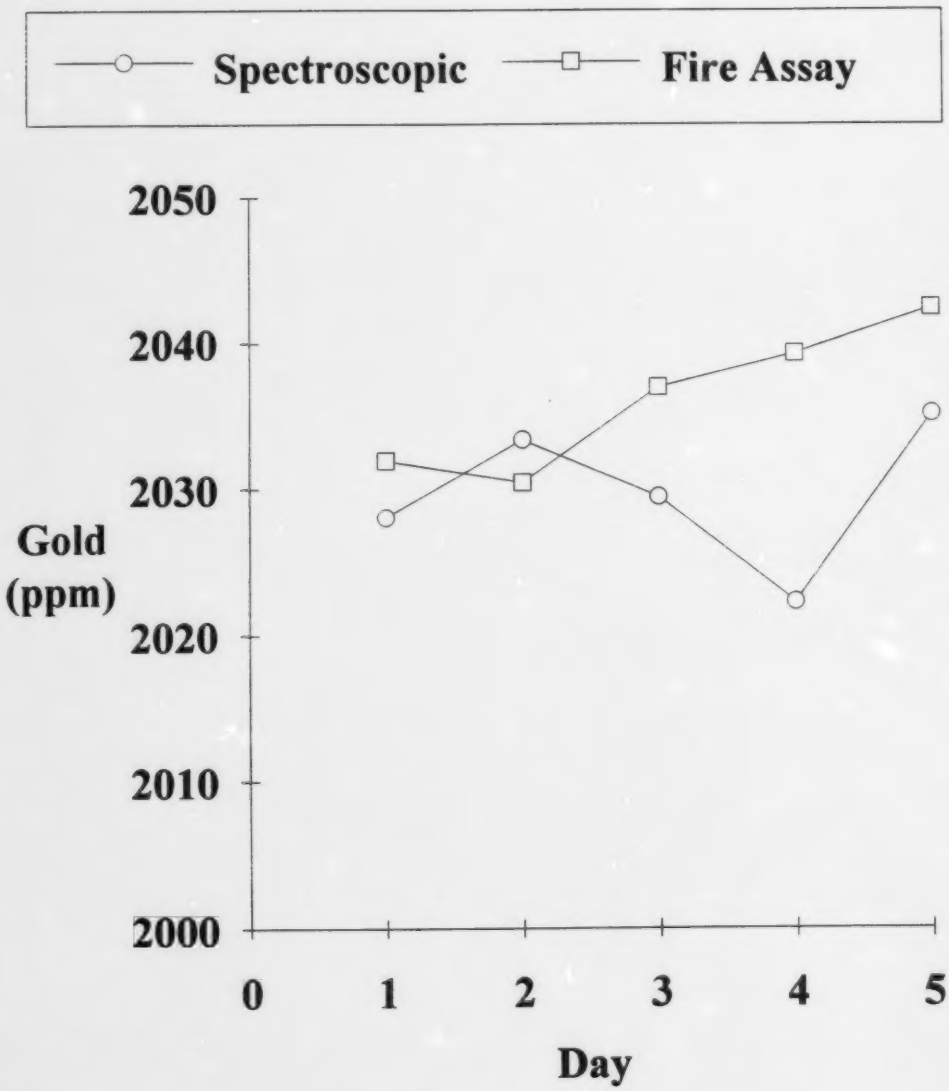

Figure 3. The Daily Variation of Au Determinations in the Copper Anode Slimes Sample, KCAS-1, by Fire Assay and Dissolution/Spectroscopic Techniques.